Docket No. 199648US0

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

IN RE APPLICATION OF: Tomoko ISHIKAWA, et al. GAU: Not Assigned

SERIAL NO: New Application EXAMINER: Not Assigned

FILED: Herewith

FOR: TONER FOR THE DEVELOPMENT OF ELECTROSTATIC IMAGE AND THE PRODUCTION PROCESS THEREOF

REQUEST FOR PRIORITY

ASSISTANT COMMISSIONER FOR PATENTS
WASHINGTON, D.C. 20231

SIR:

☐ Full benefit of the filing date of U.S. Application Serial Number, filed, is claimed pursuant to the provisions of **35 U.S.C. §120**.

☐ Full benefit of the filing date of U.S. Provisional Application Serial Number , filed , is claimed pursuant to the provisions of **35 U.S.C. §119(e)**.

■ Applicants claim any right to priority from any earlier filed applications to which they may be entitled pursuant to the provisions of **35 U.S.C. §119**, as noted below.

In the matter of the above-identified application for patent, notice is hereby given that the applicants claim as priority:

COUNTRY	APPLICATION NUMBER	MONTH/DAY/YEAR
JAPAN	11-356833	DECEMBER/16/1999
JAPAN	2000-182606	JUNE/19/2000

Certified copies of the corresponding Convention Application(s)

☐ are submitted herewith

■ will be submitted prior to payment of the Final Fee

☐ were filed in prior application Serial No. filed

☐ were submitted to the International Bureau in PCT Application Number .
Receipt of the certified copies by the International Bureau in a timely manner under PCT Rule 17.1(a) has been acknowledged as evidenced by the attached PCT/IB/304.

☐ (A) Application Serial No.(s) were filed in prior application Serial No. filed ; and

(B) Application Serial No.(s)

☐ are submitted herewith

☐ will be submitted prior to payment of the Final Fee

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[Designation of Document] Specification

[Title of the Invention] Toner for the development of electrostatic image

[Claims]

1. A toner for the development of an electrostatic image obtained by a process comprising the following two steps:

the first step wherein a particulate resin having a glass transition temperature (Tg) of 30 to 65°C and an average particle diameter of 0.1 to 1 μm is coated over a surface of a toner (core toner) having an average particle diameter of 4 to 20 μm, then the coated film is fixed or fusion-bonded; and

the second step wherein a particulate resin having a Tg of 60 to 110°C (higher than the Tg in the first step) and an average particle diameter of 0.04 to 1 μm is coated over the coated film in the first step, then the coated film is fixed or fusion-bonded.

2. The toner for the development of an electrostatic image as claimed in claim 1, wherein the particulate resin of the first step comprises 2 to 50 parts by weight of wax (based on 100 parts by weight of a base resin) encapsulated therein.

3. The toner for the development of an electrostatic image as claimed in claim 2, characterized in that the wax encapsulated in the particulate resin of the first step is one kind of resin selected from a group consisting of paraffinic

resins, olefinic resins, natural or synthetic aliphatic ester-based resins, aliphatic amide-based resins, long chain alkylketone-based resins and alkyl-modified silicone resins, or the mixture thereof, and the wax has a melting point of 50 to 95°C.

4. The toner for the development of an electrostatic image as claimed in anyone of claims 1 to 3, characterized in that a Tg of a binder resin of the core toner is 30 to 55°C.

5. The toner for the development of an electrostatic image as claimed in anyone of claims 1 to 4, wherein the base resin of the particulate resin of the first step is a copolymer resin of styrene with acrylate or methacrylate, or a terpolymer or multipolymer resin of styrene with acrylate or methacrylate and with acrylic acid or methacrylic acid.

6. The toner for the development of an electrostatic image as claimed in anyone of claims 1 to 5, wherein a base resin of the particulate resin of the second step is a copolymer resin of styrene with acrylate or methacrylate, or a terpolymer or multipolymer resin of styrene with acrylate or methacrylate and with acrylic acid or methacrylic acid.

[Detailed Description of the Invention]

[0001]

[Technical Field to which the Invention belongs]

The present invention relates to a toner for the development of an electrostatic image for use in

electrophotographic process copying machines and printers. More particularly, the present invention relates to a toner for the development of an electrostatic image having both a low temperature fixability and an oil-less fixability.

[0002]

[Related Art]

Recently, electrophotographic process copying machines and printers are intended to have a small size in order to lower a production cost and energy cost. In order to achieve such an object, it is desired to develop a toner for the development of an electrostatic image which does not require a silicone oil tank and a coating apparatus. Namely, a toner for the development of an electrostatic image having an oil-less fixability and a low temperature fixability is desired to be developed.

For achieving such a requirement, it has been attempted to lower a Tg or a melting point of a binder resin of a toner. However, the lowering of the Tg or the melting point of the binder resin of the toner invites a poor storage stability (blocking resistance) of the toner. Particularly in summer, a toner is possibly often exposed to severe conditions of up to 50°C, so it may lose its shape to be converted to a colored resin in the form of block.

[0003]

A toner for the development of an electrostatic image

having a low temperature fixability, which aims at saving energy, generally has a problem in the storage stability (blocking resistance). This low temperature fixability and the storage stability (blocking resistance) are not compatible to each other. Namely, in a case where a toner having both desirable low temperature fixability and storage stability (blocking resistance) is tried to be obtained by utilizing physical properties of a binder resin of the toner, the imparting of the low temperature fixability to the toner deteriorates the storage stability (blocking resistance) of the toner, while, the imparting of the storage stability (blocking resistance) of the toner deteriorates the low temperature fixability. In order to avoid these phenomena, have been proposed various methods, i.e., a method wherein a large amount of a synthetic ester wax is included in a toner (JP-B-2949558)(The term "JP-B" as used herein means an "examined Japanese patent publication") and a method wherein a shell having a high Tg is formed over a core having a low Tg (WO97/01131). However, a toner having sufficient performances has not been obtained yet.

[0004]

In order to satisfy the requirement for obtaining oil-less fixability, it has been tried to increase the polymerization degree of a toner binder resin to increase a viscoelasticity of a toner or to incorporate a large amount

of wax in a toner (JP-A-8-50368) (The term "JP-A" as used herein means an "unexamined published Japanese patent application"). However, in the former case, an energy cost required for fixing is high. While in the latter case, since according to kneading-grinding method, a toner to be obtained cannot comprise a sufficient amount of wax, the toner is produced according to emulsion polymerization method or suspension polymerization method. However, it is disadvantageous that the inclusion of a large amount of wax is costly.

[0005]

[Problems that the Invention is to Solve]

It is therefore an object of the present invention to overcome the difficulties of the conventional toner for the development of an electrostatic image having low temperature fixability and also the conventional toner for the development of an electrostatic image aiming at oil-less fixing, and hence provide a novel toner for the development of an electrostatic image at a low cost having both low temperature fixability and storage stability (blocking resistance) and also having oil-less fixability.

[0006]

[Means for Solving the Problems]

The present inventors have conducted extensive study and research efforts in order to solve the above-described problems. As the result, it could be found that a toner for the development

of an electrostatic image having desirable low temperature fixability and storage stability (blocking resistance) and also having an oil-less fixability could be produced by coating the surface of a toner (hereinafter, referred to as core toner) having an average particle diameter of 4 to 20 μm with two kinds of finely divided particles having a different glass transition point (Tg), respectively, by way of two steps, followed by fixing or fusion-bonding the coated films, providing slope in Tg. Thus, the present invention could be achieved.

[0007]

The essence of the present invention resides in a toner for the development of an electrostatic image obtained by a process comprising the following two steps:

the first step wherein a particulate resin having a glass transition temperature (Tg) of 30 to 65°C and an average particle diameter of 0.1 to 1 μm is coated over a surface of a toner (core toner) having an average particle diameter of 4 to 20 μm, then the coated film is fixed or fusion-bonded; and

the second step wherein a particulate resin having a Tg of 60 to 110°C (higher than the Tg in the first step) and an average particle diameter of 0.04 to 1 μm is coated over the film formed in the first step, then the coated film is fixed or fusion-bonded.

[0008]

[Mode for Carrying Out the Invention]

The present invention will be further described hereinafter.

The toner (core toner) used in the present invention may be either polymerized toner or ground toner. Namely, the toner is not specifically limited. However, in a case where a toner is intended to have a low temperature fixability, the core toner is preferably constructed by a binder resin having a Tg of 30 to 55°C. If the binder resin has a Tg of below 30°C, the core toner is difficult to be produced, and low temperature fixability and storage stability (blocking resistance) are difficult to be good balanced. While, if the binder resin has a Tg of more than 55°C, low temperature fixability is possibly deteriorated.

[0009]

The toner (core toner) to be used in the present invention can have the same construction as that of the toner generally used. As the toner, mention may be made of those obtained by kneading a binder resin, a colorant, a charge control agent and a wax, then grinding or freeze-grinding the resulting kneaded product; by suspension-polymerizing a mixture of a binder resin component monomer, a colorant, a charge control agent and a wax; by agglomerating and growing a mixture of a latex obtained by emulsion polymerization of a binder resin component monomer, a colorant, a charge control agent and a

wax, then molding the resulting aggregate to one having an optional particle size; and by agglomerating and growing a mixture of a latex having a wax encapsulated therein obtained by mixing and effecting emulsion polymerization of a binder resin component monomer and the wax, a colorant and a charge control agent, then molding the resulting aggregate to one having an optional particle size.

An average particle diameter of the core toner is 4 to 20 μm, preferably 4 to 10 μm.

[0010]

As the binder resin component which is a main component of a toner, a binder resin generally used for toner can be used. Examples of the same include polystyrene resin, polyester resin, polyacrylate resin, styrene-acrylate copolymer resin, styrene-methacrylate copolymer resin, polyvinyl chloride resin, polyvinyl acetate resin and epoxy resin.

As the colorant, those generally used for black toners and full color toners can be used. Further, the colorant may be any of inorganic or organic pigments and organic dyes, in combination as necessary. Specific examples of such a colorant include known dyes and pigments such as carbon black, nigrosine dye, aniline blue, chrome yellow, phthalocyanine blue, oil red, phthalocyanine green, hansa yellow, rhodamine dye or pigment, quinacridone, benzidine yellow, rose bengal, triallylmethane dye, monoazo dye or pigment, disazo dye or

pigment, and condensed azo dye or pigment. These dyes or pigments may be used singly or in admixture. If the toner of the present invention is a full-color toner, benzizine yellow, monoazo dye or pigment or condensed azo dye or pigment is preferably used as a yellow dye or pigment, quinacridone dye or pigment or monoazo dye or pigment is preferably used as a magenta dye or pigment, and phthalocyanine blue is preferably used as a cyan dye or pigment. The colorant is normally used in an amount of from 1 to 20 parts by weight based on 100 parts by weight of the binder resin used.

[0011]

Further, a charge control agent and a wax optionally can be used.

As the charge control agent, there may be used any known charge control agents, singly or in combination. Taking into account the adaptability to color toner (charge control agent itself is colorless or has a light color and hence doesn't impair the color tone of the toner), a quaternary ammonium salt compound is preferably used as a positively-charging charge control agent, and a metal salt or metal complex of salicylic acid or alkylsalicylic acid with chromium, zinc or aluminum, a metal salt or metal complex of benzylic acid, amide compound, phenol compound, naphthol compound, etc. are preferably used as a negatively-charging charge control agent. The amount of the charge control agent to be used may be determined by a

required chargeability of a toner. In practice, however, it is normally from 0.01 to 10 parts by weight, preferably from 0.1 to 10 parts by weight, based on 100 parts by weight of the binder resin used.

[0012]

As the wax to be used in the present invention, there may be any known wax. Examples of such a wax include paraffinic wax, olefinic wax, natural and synthetic aliphatic ester-based wax, aliphatic amide-based wax, long chain alkylketone-based wax and alkyl-modified silicone-based wax. These waxes can be used alone or in any mixture thereof. Specifically, as such a wax, mention may be made of olefinic wax such as low molecular weight polyethylene, low molecular weight polypropylene and polyethylene copolymer; natural and synthetic ester-based wax having long-chain aliphatic group; ketone having long-chain alkyl group; silicone wax having alkyl group; higher fatty acid; and higher fatty acid amide. These waxes are used in an amount of 0 to 20 parts by weight, preferably 0 to 10 parts by weight based on 100 parts by weight of a binder resin.

[0013]

In the present invention, the resin to be the base of the particulate resin in the first step has a Tg of 30 to 65°C. If the resin has the Tg of lower than 30°C, a toner obtained is to have an unstable storage stability. While, the resin having the Tg of higher than 65°C is undesirable in the balance

with an outer resin in providing a slope of Tg for imparting a low temperature fixability and an oil-less fixability.

In the present invention, the resin to be the base of the particulate resin in the second step has a Tg of 60 to 110°C which is higher than that of the first step. By fixing or fusion-bonding a resin having a high Tg as an outer shell, a blocking resistance of a resulting toner is improved.

[0014]

A kind of a resin to be a base of a particulate resin in the first step or the second step is selected, for example, from the following resins having a suitable Tg: diallyl phthalate resin (PDAP) or diallyl isophthalate resin (PDAIP) and copolymerized resin of diallyl phthalate and diallyl isophthalate (COPDAP) (they are used alone or in any mixture thereof), copolymer resin of these resins and acrylate, polystyrene resin, polyester resin, polyacrylate resin, styrene-acrylate copolymer resin, styrene-methacrylate copolymer resin, polyvinyl chloride resin, polyvinyl acetate resin, epoxy resin, styrene-acrylic acid copolymer resin, styrene-methacrylic acid copolymer resin, styrene-acrylate-acrylic acid terpolymer resin, styrene-acrylate-methacrylic acid terpolymer resin, methacrylate-acrylate-acrylic acid terpolymer resin, and methacrylate-acrylate-methacrylic acid terpolymer resin. Copolymer resin of styrene and acrylate or methacrylate, or terpolymer resin of styrene,

acrylate or methacrylate, and acrylic acid or methacrylic acid are preferably used.

[0015]

A particle diameter of the particulate resin in the first step is desirably 0.1 to 1 μm for a core toner having an average particle diameter of 4 to 20 μm, although the appropriate value differs depending upon the particle diameter of the core toner. A particle diameter of the particulate resin in the second step is desirably 0.04 to 1 μm for a core toner having an average particle diameter of 4 to 20 μm, although the appropriate value differs depending upon a particle diameter of the core toner.

An amount of the particulate resin to be used in the first step is preferably 1 to 50% by weight, more preferably 2 to 30% by weight, and the most preferably 5 to 25% by weight based on a weight of a core toner, although the amount of the particulate resin differs depending upon the balance between the particle diameter of the core toner and that of the particulate resin. If an amount of the particulate resin to be used in the first step is less than 1% by weight, the resulting toner cannot exhibit a sufficient oil-less fixability. While, if an amount of the particulate resin to be used in the first step exceeds 50% by weight, an amount of a wax to be used is increased so that a cost reduction effect is undesirably diluted, although a sufficient oil-less fixing imparting effect can be given to the resulting toner.

[0016]

An amount of the particulate resin to be used in the second step is preferably 1 to 50% by weight, more preferably 2 to 30% by weight, and the most preferably 5 to 25% by weight based on a weight of a core toner, although the amount of the particulate resin varies depending upon the balance between the particle diameter of the core toner and that of the particulate resin. If an amount of the particulate resin to be used in the second step is less than 1% by weight, the resulting toner is liable to have an insufficient storage stability (blocking resistance). While, if an amount of the particulate resin to be used in the second step exceeds 50% by weight, the resulting toner undesirably has such a tendency that an oil-less fixability cannot be exhibited sufficiently.

The particulate resin in the first step desirably comprises a wax encapsulated therein. The amount of the wax to be encapsulated is 2 to 50 parts by weight, preferably 3 to 25 parts by weight based on 100 parts of a base resin. When an amount of the wax is less than 2% by weight, the resulting toner cannot exhibit a sufficient oil-less fixability. While when the amount of the wax to be encapsulated is more than 50 parts by weight, although the oil-less fixability imparting effect can be sufficiently exhibited, the resulting toner is to have a decreased strength and an unstable storage stability. Further, an amount of the wax used is undesirably high to dilute

the cost reduction effect and the particulate resin having the wax encapsulated therein is undesirably difficult to be produced.

The particulate resin in the second step can comprise a wax encapsulated therein. However, those free from the wax is usually used.

[0017]

Wax to be used in a particulate resin can be the same as those used in the core toner. Examples of the same include paraffinic wax, olefinic wax, natural and synthetic aliphatic ester-based wax, aliphatic amide-based wax, long chain alkylketone resin-based wax and alkyl-modified silicone resin-based wax. These waxes can be used alone or in any mixture thereof. Specifically, as such a wax, mention may be made of olefinic wax such as low molecular weight polyethylene, low molecular weight polypropylene and polyethylene copolymer; natural and synthetic ester-based wax having long-chain aliphatic group; ketone having long-chain alkyl group; silicone wax having alkyl group; higher fatty acid; and higher fatty acid amide.

[0018]

A particulate resin comprising a wax encapsulated therein is produced by mixing a monomer to be a starting material of the exemplified usable base resins with the wax so that they may be dissolved optionally by heating,

successively adding an emulsifier and a polymerization initiator to the resulting product, followed by effecting conventional emulsion polymerization, whereby particulate resin latex comprising the wax encapsulated therein is produced.

A method for coating a particulate resin, then fixing or fusion-bonding the coated film comprises adding a particulate resin dispersion in the first step to a dispersion of a core toner so that the particulate resin is adhered to the core toner by utilizing electrostatic adhesion in the case of different polarity or by utilizing suction force among particles in the case of the same polarity, and optionally adjusting pH or electrical conductivity, whereby a film is formed, which is then fixed or fusion-bonded by a thermal treatment. In the fixing or fusion-bonding, if necessary, also can be employed a treatment wherein a pH regulation or an electrical conductivity regulation is effected again to prevent toner particles from agglomeration.

[0019]

[Examples]

The present invention will be further described in the following examples.

The term "parts" as used hereinafter is meant to indicate "parts by weight".

(1) Production of core toner

(1-A) Kneading-grinding method toner

Styrene/acrylic resin	100 parts
(produced by Sekisui Kagaku k.K., trade name MK-9472, MW 34,000, Tg 30°C)	
Cyan pigment EP700	6 parts
Paraffin wax	5 parts
Charge control agent P-51	2 parts

These ingredients were kneaded through a biaxial extruder PCM30 (manufactured by Ikegai Tekkojyo), then the resulting kneaded product was ground and classified to obtain toner (A) having an average particle diameter of 8.4 μm.

[0020]

(1-B) Kneading-grinding method toner

Styrene/acrylic resin	100 parts
(produced by Sekisui Kagaku k.K., trade name MK-9407, MW 34,000, Tg 50°C)	
Cyan pigment EP700	6 parts
Paraffin wax	5 parts
Charge control agent P-51	2 parts

These ingredients were kneaded through a biaxial extruder PCM30 (manufactured by Ikegai Tekkojyo), then the resulting kneaded product was ground and classified to obtain toner (B) having an average particle diameter of 9.1 μm.

[0021]

(1-C) Emulsion polymerization agglomeration toner slurry

Latex (MW 54,000, resin Tg 40°C, resin concentration 20wt%) produced by emulsifying a monomer mixture of styrene/butyl acrylate/acrylic acid = 59/39/2 with sodium dodecylbenzene sulfonate, followed by effecting emulsion polymerization using hydrogen peroxide as an initiator. 500 parts

Cyan pigment EP700 dispersion (solid content concentration 35 wt%) 17 parts

Paraffin wax (LUVAX-1266 produced by Nippon Seirou) emulsified product (solid content concentration 25 wt%) 20 parts

MCN13NK dispersion (solid content concentration 5 wt%) 12 parts

These ingredients were mixed with stirring and regulated to have a pH of 3.5. Successively, the resulting mixture was heated at a rate of 1°C/min. while the particle size was sometimes measured. At a time when the particle diameter reached 5.5 μm, the mixture was regulated to have a pH of 7, whereby the particle diameter growth was stopped, and further kept at 60°C for 1 hour and cooled. Thus, agglomerated toner slurry (solid content concentration 22.3%) (C) was obtained.

[0022]

(1-D) Emulsion polymerization agglomeration toner

A part of the agglomerated toner slurry (solid content concentration 22.3%) obtained in (C) was filtered, washed and dried to obtain agglomerated toner (D).

(1-E)

Styrene	60 parts
Butyl acrylate (2-ethylhexyl acrylate)	39.6 parts
Divinyl benzene	0.4 parts
Carbon black MA100S (produced by Mitsubishi Kasei K.K.)	4 parts
Paraffin wax (LUVAX-1266 produced by Nippon Seirou)	5 parts
Dispersant Disparon (produced by Kushimoto Kasei)	1.5 parts
Polymerization initiator V-65 [(2,2'-azobis(2,4-dimethylvaleronitrile) produced by Wako Junyaku]	5 parts

These ingredients were mixed and dispersed by a conventional method to prepare a monomer mixture. Separately, a mixed dispersion comprising:

Calcium triphosphate	25 parts
Sodium polyacrylate	0.05 parts
Calcium chloride	200 parts
Desalted water	300 parts

was prepared. To this mixed dispersion was added the above-prepared monomer mixture to prepare a suspension. The suspension obtained was subjected to suspension polymerization according a conventional method, then washed with an acid, filtered, washed with water and dried. Thus,

could be obtained suspension polymerization toner (E) having a MW of 33,000, a resin Tg of 40°C and a particle diameter of 6.9 μm.

[0023]

(1-F) Suspension polymerization toner

Suspension polymerization was effected according to the same manner as in (1-E) except that the monomer mixture composition was changed to the following composition comprising:

Styrene	67 parts
Butyl acrylate (2-ethylhexyl acrylate)	32.6 parts
Divinyl benzene	0.4 parts
Carbon black MA100S (produced by Mitsubishi Kasei K.K.)	4 parts
Paraffin wax (LUVAX-1266 produced by Nippon Seirou)	5 parts
Dispersant Disparon	1.5 parts
Polymerization initiator V-65 [(2,2'-azobis(2,4-dimethylvaleronitrile) produced by Wako Junyaku]	5 parts

Thus, could be obtained suspension polymerization toner (F) having a MW of 32,000, a resin Tg of 50°C and a particle diameter of 8.2 μm.

[0024]

(2) Production of particulate resin (particulate resin

comprising wax encapsulated therein) of first step

(2-G) Particulate resin comprising paraffin wax encapsulated therein

A 10 parts amount of paraffin wax (LUVAX-1266 produced by Nippon Seirou) was uniformly dissolved in 90 parts of a monomer mixture of styrene/butyl acrylate/acrylic acid = 75.2/22.8/2, which was emulsified with sodium dodecylbenzene sulfonate. The resulting emulsion was subjected to emulsion polymerization using hydrogen peroxide as an initiator. Thus, particulate resin latex comprising the paraffin wax encapsulated therein (G) having a MW of 74,000, a resin Tg of 65°C and an average particle diameter of 0.206 μm and a resin concentration of 20 wt% could be obtained.

[0025]

(2-H) Particulate resin comprising ester-based wax encapsulated therein

A 10 parts amount of ester wax (Unister M2222SL produced by Nippon Yushi) was uniformly dissolved in 90 parts of a monomer mixture of styrene/butyl acrylate/acrylic acid = 75.2/22.8/2, which was emulsified with sodium dodecylbenzene sulfonate. The resulting emulsion was subjected to emulsion polymerization using hydrogen peroxide as an initiator. Thus, particulate resin latex comprising the ester wax encapsulated therein (H) having a MW of 71,000, a resin Tg of 65°C and an average particle diameter of 0.254 μm and a resin concentration

of 20 wt% could be obtained.

[0026]

(2-I) Particulate resin comprising ester-based wax encapsulated therein

A 10 parts amount of ester wax (Unister M2222SL produced by Nippon Yushi) was uniformly dissolved in 90 parts of a monomer mixture of styrene/butyl acrylate/acrylic acid = 72/26/2, which was emulsified with sodium dodecylbenzene sulfonate. The resulting emulsion was subjected to emulsion polymerization using hydrogen peroxide as an initiator. Thus, particulate resin latex comprising the ester wax encapsulated therein (I) having a MW of 69,000, a resin Tg of 60°C and an average particle diameter of 0.244 μm and a resin concentration of 20 wt% could be obtained.

[0027]

(2-J) Particulate resin comprising ester-based wax encapsulated therein

A 20 parts amount of ester wax (Unister M2222S1 produced by Nippon yushi) was uniformly dissolved in 80 parts of a monomer mixture of styrene/butyl acrylate/acrylic acid = 72/26/2, which was emulsified with sodium dodecylbenzene sulfonate. The resulting emulsion was subjected to emulsion polymerization using hydrogen peroxide as an initiator. Thus, particulate resin latex comprising the ester wax encapsulated therein (J) having a MW of 54,000, a resin Tg of 60°C and a

particle diameter of 0.206 μm and a resin concentration of 20 wt% could be obtained.

[0028]

(3) Production of particulate resin of second step

(3-K) ME-300 produced by Soken Kagaku

(Polymethyl methacrylate particulate resin emulsion, resin concentration 23.6 wt%, Tg 105°C, MW 500,000 and average particle diameter 0.1 μm)

(3-L) DAP-SPHD-E produced by Daiso K.K.

(Copolymer resin emulsion of diallyl phthalate and acrylate, resin concentration 40 wt%, Tg 90°C and average particle diameter 0.1 μm)

(3-M) Styrene/acrylate particulate resin

A monomer mixture of styrene/butyl acrylate/acrylic acid = 75.2/22.8/2 was emulsified with sodium dodecylbenzene sulfonate. The resulting emulsion was subjected to emulsion polymerization using hydrogen peroxide as an initiator. Thus, particulate resin latex (M) having a MW of 74,000, a resin concentration of 20wt%, a resin Tg of 65°C and an average particle diameter of 0.078 μm could be obtained.

(3-N) ME-5015 produced by Soken Kagaku

(Copolymer resin emulsion of styrene/methyl methacrylate/acrylic acid, MW 396,000, resin concentration 25.1 wt%, resin Tg 107°C, and average particle diameter 0.13 μm)

[0029]

(3-O) SE-A produced by Soken Kagaku

(Copolymer resin emulsion of styrene/butyl acrylate/acrylic acid, MW 88,000, resin concentration 20.5 wt%, resin Tg 65°C, and average particle diameter 0.1 μm)

[0030]

(4) Fixability determination method

Test was effected at various temperatures using a fixing machine (fixing roller Φ 35 mm) for a copying machine JX-8200 produced by Sharp K.K., at a process speed of 120 mm/sec and a nip width of 4 mm without using silicone oil.

[0031]

(5) Evaluation method of blocking resistance

Cartridge paper uniformly cut to a length of about 55 mm is rounded into a cylindrical shape and set inside a cylinder having an inner diameter of 30 mm formed by clamping two sheets of half pipes having a length of 50 mm with a rubber band, which is placed on a magnetic flat plate. Then, 10 g of a toner is weighted into the cylindrical cartridge paper. The toner is weighted carefully in such a manner that the upper part thereof may be formed as flat as possible. Successively, a weight having a flat bottom, a bottom diameter of 27 mm and a weight of 20 g is carefully placed on the toner in such a manner that the toner is not scattered out, which is then allowed to stand in an atmosphere of 50°C and 50%RH for 5 hours, followed by

cooling to room temperature. Successively, the weight, the cartridge paper, and the half pipe are removed to prepare a cylindrical blocking resistance evaluation sample. Then, a sinker is placed on the cylindrical sample obtained and blocking resistance is evaluated by a weight of the sinker (g or kg) at a time when the cylindrical sample is broken.

Judgements are as follows.

◎: 0 g to 200 g, O: 200 g < ~500 g, Δ: 500 g< ~1 kg, X: 1 kg< ~3 kg, XX: 3 kg < ~5 kg <

[0032]

[Example 1]

<First step reaction>

Particulate resin latex comprising wax encapsulated therein (G)

50 parts

Desalted water 600 parts

were charged into a reaction container, then

Toner (A) 100 parts

was gradually added thereto at room temperature with stirring by means of a flat-blade agitator at a velocity of 300 to form a uniform dispersion. Successively, pH of the dispersion was adjusted to 3.0 with stirring to effect reaction until the white-turbidity of the dispersion disappeared. Then, the reaction temperature was elevated to 35°C and the reaction was continued for 2 hours, whereby the first step particulate resin

was fixed to a core toner, followed by cooling to room temperature.

[0033]

<Second step reaction>

Successively, 42 parts of ME-300(K) emulsion produced by Soken Kagaku was added to the resulting product, then, pH of the mixture (dispersion) obtained was adjusted to 2.0 to effect reaction until the white-turbidity of the dispersion disappeared. Successively, the reaction temperature was elevated to 35°C and the reaction was effected for 2 hours and, further, the reaction temperature was stepwise elevated to 65°C and the reaction was continued for 2 hours, whereby the second step particulate resin was fixed to the above-described product, followed by cooling to room temperature. Then, the resulting product was filtered, washed with water and dried, whereby the second step particulate resin-fixed toner was obtained.

By using this particulate resin-fixed toner, an unfixed image was formed by means of a two component-system copying machine (DC-2355 produced by Mita Kogyo). Then, oil-less fixability was evaluated using a fixing machine, which has been reconstructed so that the temperature might be optionally controlled, for a commercially available copying machine (JK-8200 produced by Sharp K.K.). As the result, it could be confirmed that the toner was fixed in a temperature range of 115 to 155°C.

[0034]

[Example 2]

<First step reaction>

Particulate resin latex comprising wax encapsulated therein (H)

50 parts

Desalted water 600 parts

were charged into a reaction container, then

Toner (B) 100 parts

was gradually added thereto at room temperature with stirring by means of a flat-blade agitator at a velocity of 300 to form a uniform dispersion. Successively, pH of the dispersion was adjusted to 3.0 with stirring to effect reaction until the white-turbidity of the dispersion disappeared. Then, the reaction temperature was elevated to 50°C and the reaction was continued for 2 hours, whereby the first step particulate resin was fixed to a core toner, followed by cooling to room temperature.

[0035]

<Second step reaction>

Successively, 30 parts of styrene/acryl-based particulate resin (M) emulsion produced by emulsion polymerization was added to the resulting product, then, pH of the mixture (dispersion) obtained was adjusted to 2.0 to effect reaction until the white-turbidity of the dispersion disappeared.

Successively, the reaction temperature was stepwise elevated to 50°C and the reaction was effected for 2 hours and, further, the reaction temperature was stepwise elevated to 60°C and the reaction was continued for 2 hours, whereby the second step particulate resin was fixed to the above-described product, followed by cooling to room temperature. Successively, the resulting product was filtered, washed with water and dried, whereby the second step particulate resin-fixed toner was obtained.

By using this particulate resin-fixed toner, an unfixed image was formed by means of a two component-system copying machine (DC-2355 produced by Mita Kogyo). Then, oil-less fixability was evaluated using a fixing machine, which has been reconstructed so that the temperature might be optionally controlled, for a commercially available copying machine (JK-8200 produced by Sharp K.K.). As the result, it could be confirmed that the toner was fixed in a temperature range of 130 to 165°C.

[0036]

[Example 3]

Particulate resin latex comprising wax encapsulated therein (I)

50 parts

Desalted water 600 parts

were charged into a reaction container, then

Toner (C) 100 parts

was gradually added thereto at room temperature with stirring by means of a flat-blade agitator at a velocity of 300 to form a uniform dispersion. Successively, pH of the dispersion was adjusted to 3.0 with stirring to effect reaction until the white-turbidity of the dispersion disappeared. Then, the reaction temperature was elevated to 40°C and the reaction was continued for 2 hours, whereby the first step particulate resin was fixed to a core toner, followed by cooling to room temperature.

[0037]

<Second step reaction>

Successively, 50 parts of DAP-SPHD-E(L) emulsion produced by Diso K.K. was added to the resulting product, then, pH of the mixture (dispersion) obtained was adjusted to 2.0 to effect reaction until the white-turbidity of the dispersion disappeared. Successively, the reaction temperature was stepwise elevated to 40°C and the reaction was effected for 2 hours and, further, the reaction temperature was stepwise elevated to 60°C and the reaction was continued for 2 hours, whereby the second step particulate resin was fixed to the above-described product, followed by cooling to room temperature. Successively, the resulting product was filtered, washed with water and dried, whereby the second step particulate resin-fixed toner was obtained.

By using this particulate resin-fixed toner, an unfixed image was formed by means of a two component-system copying machine (DC-2355 produced by Mita Kogyo). Then, oil-less fixability was evaluated using a fixing machine, which has been reconstructed so that the temperature might be optionally controlled, for a commercially available copying machine (JK-8200 produced by Sharp K.K.). As the result, it could be confirmed that the toner was fixed in a temperature range of 120 to 165°C.

[0038]

[Example 4]

Agglomerated toner slurry (D-1) (solid concentration 22.3%)

450 parts

Particulate resin latex comprising wax encapsulated therein (I)

50 parts

were charged into a reaction container, then pH of the mixture (dispersion) was adjusted to 3.0 with stirring at room temperature by means of a flat-blade agitator at a velocity of 300 to effect reaction until the white-turbidity of the dispersion disappeared. Then, the reaction temperature was elevated to 40°C and the reaction was continued for 2 hours, whereby the first step particulate resin was fixed to a core toner, followed by cooling to room temperature.

[0039]

<Second step reaction>

Successively, 50 parts of DAP-SPHD-E(L) emulsion produced by Diso K.K. was added to the resulting product, then, pH of the mixture (dispersion) obtained was adjusted to 2.0 to effect reaction until the white-turbidity of the dispersion disappeared. Successively, the reaction temperature was stepwise elevated to 40°C and the reaction was effected for 2 hours and, further, the reaction temperature was stepwise elevated to 60°C and the reaction was continued for 2 hours, whereby the second step particulate resin was fixed to the above-described product, followed by cooling to room temperature. Successively, the resulting product was filtered, washed with water and dried, whereby the second step particulate resin-fixed toner was obtained.

[0040]

By using this particulate resin-fixed toner, an unfixed image was formed by means of a two component-system copying machine (DC-2355 produced by Mita Kogyo). Then, oil-less fixability was evaluated using a fixing machine, which has been reconstructed so that temperature might be optionally controlled, for a commercially available copying machine (JK-8200 produced by Sharp K.K.). As the result, it could be confirmed that the toner was fixed in a temperature range of 120 to 165°C.

[0041]

[Example 5]

Particulate resin latex comprising wax encapsulated therein (I)

50 parts

Desalted water 600 parts

were charged into a reaction container, then

Toner (E) 100 parts

was gradually added thereto at room temperature with stirring by means of a flat-blade agitator at a velocity of 300 to form a uniform dispersion. Successively, pH of the dispersion was adjusted to 3.0 with stirring to effect reaction until the white-turbidity of the dispersion disappeared. Then, the reaction temperature was elevated to 40°C and the reaction was continued for 2 hours, whereby the first step particulate resin was fixed to a core toner, followed by cooling to room temperature.

[0042]

<Second step reaction>

Successively, 39 parts of SE-A(O) emulsion produced by Soken Kagaku was added to the resulting product, then, pH of the mixture (dispersion) obtained was adjusted to 2.0 to effect reaction until the white-turbidity of the dispersion disappeared. Successively, the reaction temperature was elevated to 40°C and the reaction was effected for 2 hours and, further, the reaction temperature was stepwise elevated to 60°C

and the reaction was continued for 2 hours, whereby the second step particulate resin was fixed to the above-described product, followed by cooling to room temperature. Successively, the resulting product was filtered, washed with water and dried, whereby the second step particulate resin-fixed toner was obtained.

By using this particulate resin-fixed toner, an unfixed image was formed by means of a two component-system copying machine (DC-2355 produced by Mita Kogyo). Then, oil-less fixability was evaluated using a fixing machine, which has been reconstructed so that the temperature might be optionally controlled, for a commercially available copying machine (JK-8200 produced by Sharp K.K.). As the result, it could be confirmed that the toner was fixed in a temperature range of 120 to 160°C.

[0043]

[Example 6]

Particulate resin latex comprising wax encapsulated therein (J)

50 parts

Desalted water 600 parts

were charged into a reaction container, then

Toner (F) 100 parts

was gradually added thereto at room temperature with stirring by means of a flat-blade agitator at a velocity of 300 to form

a uniform dispersion. Successively, pH of the dispersion was adjusted to 3.0 with stirring to effect reaction until the white-turbidity of the dispersion disappeared. Then, the reaction temperature was elevated to 50°C and the reaction was continued for 2 hours, whereby the first step particulate resin was fixed to a core toner, followed by cooling to room temperature.

[0044]

<Second step reaction>

Successively, 20 parts of ME-5015(N) emulsion produced by Soken Kagaku was added to the resulting product, then, pH of the mixture (dispersion) obtained was adjusted to 2.0 to effect reaction until the white-turbidity of the dispersion disappeared. Successively, the reaction temperature was elevated to 50°C and the reaction was effected for 2 hours and, further, the reaction temperature was stepwise elevated to 65°C and the reaction was continued for 2 hours, whereby the second step particulate resin was fixed to the above-described product, followed by cooling to room temperature. Successively, the resulting product was filtered, washed with water and dried, whereby the second step particulate resin-fixed toner was obtained.

By using this particulate resin-fixed toner, an unfixed image was formed by means of a two component-system copying machine (DC-2355 produced by Mita Kogyo). Then, oil-less

fixability was evaluated using a fixing machine, which has been reconstructed so that the temperature might be optionally controlled, for a commercially available copying machine (JK-8200 produced by Sharp K.K.). As the result, it could be confirmed that the toner was fixed in a temperature range of 130 to 175°C.

[0045]

[Comparative Example 1]

Evaluation of fixability was effected using toner (A) according to the same manner as that of Example 1. As the result, it was confirmed that offset occurred in a temperature range of 100 to 200°C (Evaluation was not effected at a temperature of 200°C or more.).

[0046]

[Comparative Example 2]

Evaluation of fixability was effected using toner (B) according to the same manner as that of Example 2. As the result, it was confirmed that offset occurred in a temperature range of 120 to 200°C (Evaluation was not effected at a temperature of 200°C or more.).

[0047]

[Comparative Example 3]

Evaluation of fixability was effected using toner (C) according to the same manner as that of Example 3. As the result, it was confirmed that the toner was fixed in a narrow

temperature range of 110 to 125°C. It was also confirmed that offset occurred in a temperature range of more than 125 to 200°C (Evaluation was not effected at a temperature of 200°C or more.).

[0048]

[Comparative Example 4]

Evaluation of fixability was effected using toner (D) according to the same manner as that of Example 4. As the result, it was confirmed that the toner was fixed in a narrow temperature range of 110 to 125°C. It was also confirmed that offset occurred in a temperature range of more than 125 to 200°C (Evaluation was not effected at a temperature of 200°C or more.).

[0049]

[Comparative Example 5]

Evaluation of fixability was effected using toner (E) according to the same manner as that of Example 5. As the result, it was confirmed that the toner was fixed in a narrow temperature range of 115 to 125°C. It was also confirmed that offset occurred in a temperature range of more than 125 to 200°C (Evaluation was not effected at a temperature of 200°C or more.).

[0050]

[Comparative Example 6]

Evaluation of fixability was effected using toner (F)

according to the same manner as that of Example 6. As the result, it was confirmed that the toner was fixed in a narrow temperature range of 125 to 130°C. It was also confirmed that offset occurred in a temperature range of more than 125 to 200°C (Evaluation was not effected at a temperature of 200°C or more.).

Results of Examples and those of Comparative Examples are shown together in Table 1 below.

[0051]

[Table 1]

Table 1 Fexability and blocking resistance

Example and Comparative Example No.	Oil-less fixing region (°C)	Storage stability
Example 1	115 to 155	O
Example 2	130 to 165	◎
Example 3	120 to 165	◎
Example 4	120 to 165	◎
Example 5	120 to 160	O
Example 6	130 to 175	◎
Comparative Example 1	None	XX
Comparative Example 2	None	Δ
Comparative Example 3	None	X
Comparative Example 4	110 to 125	X
Comparative Example 5	115 to 125	X
Comparative Example 6	125 to 130	Δ

[0054]

[Effect of the Invention]

According to the method of the present invention, can be readily produced a toner having desirable low temperature fixability and storage stability (blocking resistance), and also having oil-less fixability.

[Designation of Document] Abstract of the Disclosure

[Abstract]

[Problem] Provision of a toner for the development of an electrostatic image excellent in oil-less fixability at a low cost

[Means for Resolution] A toner for the development of an electrostatic image obtained by a process comprising the following two steps:

the first step wherein a particulate resin preferably comprising wax encapsulated therein, and having a glass transition temperature (Tg) of 30 to 65°C and an average particle diameter of 0.1 to 1 μm is coated over a surface of a toner (core toner) comprising a binder resin having an average particle diameter of 4 to 20 μm and Tg of preferably 30 to 55°C, then the coated film is fixed or fusion-bonded; and

the second step wherein a particulate resin having a Tg of 60 to 110°C and an average particle diameter of 0.04 to 1 μm is coated over the coated film in the first step, then the coated film is fixed or fusion-bonded. The resulting toner is excellent in low temperature fixability and oil-less fixability.

[Selected Drawing] None